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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Jin	Sungho	San Diego, California

☐ *Additional inventors are being named on the ____ separately numbered sheets attached hereto*

TITLE OF THE INVENTION (280 characters max)

ARTICLE COMPRISING UNIVERSAL SOLDERS AND METHOD FOR FABRICATING SUCH ARTICLE

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

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ENCLOSED APPLICATION PARTS *(check all that apply)*

☒ Specification *Number of Pages* 9
☐ Drawing(s) *Number of Sheets*
☐ Application Data Sheet. See 37 CFR 1.76
☐ CD(s), Number
☐ Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT *(check one)*

☒ Applicant claims small entity status. See 37 CFR 1.27.
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.
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Respectfully submitted,

SIGNATURE Glen E Books

Date 04/09/2003

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USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

Article Comprising Universal Solders and Method for Fabricating Such Article

Inventor: Sungho Jin, Professor of Materials Science, University of California at San Diego, La Jolla, CA 92093-0411, (T) 858-534-4903, (F) 858-534-5698, (e) jin@ucsd.edu

FIELD OF THE INVENTION

The present invention relates to reactive solders and brazes and, in particular, to solder and braze materials containing rare earth elements. The inventive solder and braze materials are particularly useful for direct bonding onto non-metallic surfaces such as oxides, nitrides or diamond.

BACKGROUND OF THE INVENTION

Solders and brazes are often used for such bonding, and they include metallic compositions consisting of an elemental-metal or an alloy-metal matrix. The metallic matrices of solders have conveniently low melting temperatures, i.e., lower than about 450°C. The metallic matrices of brazes have higher melting temperatures than those of solders, and thus, form more thermally resistant bonds.

For construction of modern optical, MEMS and electronic devices, reliable bonding of dissimilar materials involving such oxides, nitrides, carbides, semiconductors, Al or Ti metallization surfaces, metallic components, and diamonds is often one of the essential fabrication steps. It is well known that low-melting-temperature solders such as Pb-Sn, Sn-Ag, Bi-Sn, and Au-Sn do not wet and bond to these surfaces

Solders such as Pb-Sn, Sn-Ag, Bi-Sn, and Au-Sn are widely used for bonding of components and circuits in electronic and optoelectronic devices. Numerous other solder compositions, as well as a variety of processing and assembly procedures, are also known. See a book by H. H. Manko, *Solders and Soldering*, McGraw-Hill Inc. (1992).

Widely-used optical components, MEMS devices, and electronic components are made up of a variety of inorganic materials such as oxides, nitrides, carbides, fluorides, semiconductors, metals, and diamonds. For construction and packaging of modern optical, MEMS and electronic devices, reliable bonding of dissimilar materials is often one of the essential fabrication steps. Lasers and other optoelectronic components as well as optical fibers for telecommunication networks need to be bonded on an assembly substrate with sub-micron accuracy and stability in alignment with respect to each other in order to ensure and maximize optical signal transmission. MEMS chips, especially those based on silicon-on-insulator (SOI) fabrication approaches, need to be bonded with a certain spatial configuration relative to the separate actuator electrode layers, often desirably in hermetic seal environment, such as disclosed by U.S. Patent No. 6,442,307, August 27, 2002, "Solder-packaged optical MEMs device and method for making the same" by D. W. Carr, et al.

Completed optical or RF switch MEMS devices, optical packages, and electronic packages often require hermetic sealing to shield them from environmental effects of humidity, air damping and other factors. Electronic devices generally contain base semiconductor materials (such as Si, GaAs, GaN, SiC, doped-diamond), diffusion barriers (such as TiN, TaN), dielectrics (such as SiO_2, Ta_2O_5, Si_3N_4), electrical conductors (such as Al, W, Cu, $CoSi_2$) as well as heat sink materials (such as Al, AlN, diamond). A variety of electrical paths, lead wire contact bonds, and mechanical bondings are made at different packaging levels. Semiconductors and associated circuits need to be connected to other components. See a book by R. R. Tummala, E. J. Rymaszewski, and A. G. Klopfenstein, *Microelectronics Packaging Handbook*, 2nd Edition, Chapman & Hall, 1997.

Low-melting-temperature solders do not wet and bond to the surfaces of oxides, nitrides, carbides, fluorides, semiconductors, and diamonds. While solder bonding to these materials can in principle be accomplished by adding extra multilayer metallizations (often requiring an adhesion layer + diffusion barrier layer + solderable surface layer, for example, Ti/Pt/Au sputter deposited coatings), the introduction of these multilayers often causes production complications/delays, additional costs, diminished flexibility in manufacturing process options, and possible reliability complications. In MEMS devices, for example, thin film coatings usually cause stresses and undesirable warping/curving of thin Si membranes. Optical telecom fibers (SiO_2) have to be placed in a plating bath for electrochemical coating (e.g., with Ni) or cut short to be placed inside a sputtering vacuum chamber to provide solderable metallizations. Ni coating often used on fibers provides only weak, hoop-stress type adherence, with some reliability concerns. For convenience and simplicity of device assembly in manufacturing as well as for reliability and broadened design capabilities, it is desirable to find a way of achieving a direct and strong bonding onto these electronic, optical, MEMS and other inorganic materials. The surfaces of nitrides, carbides, oxides, sulfides, fluorides, selenides, diamonds, silicon, GaAs and GaN are known to be very difficult to directly bond with low temperature solders.

The incorporation of rare earth elements into solders allows a direct and powerful bonding, without flux or metallization layers, on these non-solderable surfaces, as disclosed in US Patents No. 6,306,516 by S. Jin et al., "Article comprising oxide-bondable solder" issued on October 23, 2001, No. 6,319,617 by S. Jin et al., "Oxide-bondable solder" issued on November 20, 2001, and US Patent Application No. 20020106528 by S. Jin et al., "Oxidation-resistant reactive solders and brazes" filed on August 8, 2002. These solders are truly "universal" in that they bond to essentially all inorganic surfaces. However, these solders are prone to oxidation, and therefore an improved solder structures and application techniques are needed for more practical use of these special solders. In this invention, such desirably improved universal solder materials and bonding techniques are disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

The nature, advantages and various additional features of the invention will appear more fully upon consideration of the illustrative embodiments now to be described in detail with the accompanying drawings. In the drawings:

Fig. 1 schematically illustrates various universal solder configurations.
Fig. 2 is a schematic illustration of vertical interconnection using universal solder bonding.
Fig. 3 schematically illustrates a technique for rapid application of universal solder by (a)hot wire brush, (b)doctor blade according to the invention.
Fig. 4 schematically illustrates a controlled collapse joining with universal solder.
Fig. 5 schematically shows localized heaters for controlled collapse joining with universal solder.

Fig. 6 schematically illustrates an assembly of SOI layers with universal solder joints for optical MEMS.
Fig. 7 illustrates a hermetic sealing for optical MEMS.
Fig. 8 schematically illustrates optical fiber bonding for (a) fiber positioning in alignment with laser beam, (b) temperature-compensators, (c) wavelength-tunable fiber grating filter device.

It is to be understood that the drawings are for purposes of illustrating the concepts of the invention and are not to scale.

DETAILED DESCRIPTION

(a)

It is well known that low-melting-temperature solders, such as Pb-Sn, Sn-Ag, Au-Sn eutectic, do not wet and bond to the surfaces of oxides, nitrides, carbides, fluorides, diamonds, and semiconductors. This is due to the stability of these substrate materials involved, and hence the lack of chamical reactions between the stable surface and the molten solder material. In order to enable solder wetting and bonding on such non-wettable surfaces, we selected some of the most reactive elements in the periodic table, i.e., the rare earth elements. The solders, when doped with just a few percent of the rare earth (RE) elements such as Lu, Er, Ce, exhibits strong bonding to essentially all inorganic surfaces, and hence is named "Universal Solders".

The relative stability of the substrate material to be bonded vs that of the rare earth is the key to the successful chemical bonding to occur. For example, consider the case of universal solder bonding to the widely used optical communications fiber glass, SiO_2. The rare earth containing compounds such as RE-carbide, -nitride, -oxide, -fluoride, -sulfide, etc. are thermodynamically favorable [9,10] as the heat of formation ($-\Delta H_f$) of rare earth compounds tends to be greater (more negative) than those for most of the non-RE metal carbides, nitrides, oxides, fluorides and sulfides. For example, Lu_2O_3 and Er_2O_3 have very large negative values of heat of formation ΔH_f (Lu_2O_3) of -282 Kcal/mole and ΔH_f (Er_2O_3) of -290 Kcal/mole, respectively, at ~298°K, as compared to ΔH_f (SiO_2) of -195 Kcal/mole. Therefore the reaction of the rare earth-containing solder with the SiO_2 surface is expected to proceed as a reaction; Lu (in molten solder) + SiO_2 (Opt. Fiber) $\Rightarrow$ Lu_2O_3 + Si. The chemical reaction so induced accounts for the observed strong bonding between the rare-earth-doped solder and the surfaces of oxides, nitrides, carbides, etc.

While the presence of very reactive rare earth element allows such direct bonding, the universal solders are susceptible to oxidation during solder bonding process because of the very same reason, i.e., having rare earth elements. Rapid oxidation of rare earth on the surface of molten universal solders is a non-trivial problem, which tends to deteriorate the solder wetting characteristics if not carefully processed. The reactive elements used in universal solders easily oxidize and tend to cause oxide skins with high melting points (e.g., ~2300°C) to form on the solders and brazes when heated or melted. The oxide skins prevent universal solders from wetting surfaces to be bonded. Another effect of the oxide skins interfering with the bonding is the impeding of the diffusion of rare earth atoms from the interiors of solder to the interface to be bonded. Thus, the prevention of the formation of oxide skins is crucial for broad and successful applications of the universal solders.

In order to prevent/minimize such oxide skins, the following some novel approaches may be utilized to modify the composition and structure of the universal solders — surface novel metal film deposition, jacketing with regular solder to bury RE underneath the solder surface, dip-coating with regular solder to bury RE underneath, or burying RE underneath by ion implantation. Such modifications are described in the aforementioned US Patent Application No. 20020106528 by S. Jin et al.

To briefly describe, a thin novel metal coating of Ag or Au can be applied onto the surface of solder perform or solder powders in order to minimize the oxidation of universal solder surface. Frequently used solders such as Au-Sn or Sn-Ag eutectic already contain Au or Ag, so the addition of surface novel metal film basically does not affect the solder chemistry except for slight enrichment which can of course be compensated if needed by adjusting base solder composition toward slight deficiency in the novel metal content. Au or Ag coating can protect/minimize the universal solders from oxidation during heating and soldering operations, and then easily dissolves into the solder so that the solder-substrate bonding takes place.

The desired coating thickness would depend on the time and temperature involved in the soldering operations, basically requiring a sufficient thickness to minimize and block the diffusion of rare earth atoms to the very surface to form an oxide layer. For certain applications, the solder bonding using universal solders can beneficially be carried out in vacuum or inert atmosphere, if industrially acceptable, to cut off the source of oxygen and prevent/minimize oxidation. Such novel metal coating can be accomplished by physical vapor deposition such as sputtering or evaporation, or by electrolytic plating or electroless deposition of Au or Ag on universal solder surface. A modified solder structures with gradient or buried rare earth distribution can also be utilized, e.g., by sandwiching (jacketing) the universal solder sheet with regular RE-free solder sheets or wrapping with annealed Au or Ag foil, and then cold welding them together, e.g., by using plastic deformation via cold rolling or pressing.

Oxidation-resistant universal solders with buried rare earth underneath the solder surface can also be produced by by dip-coating the universal solder sheet with molten regular solder. Yet another way structuring the universal solder with buried rare earth is by inserting the RE element underneath the solder surface through ion implantation.

Instead of structural modifications, novel processing approaches alone or in combination with the structural modifications can be utilized to minimize surface oxidation of rare earth element on the molten universal solder surface and produce strong solder bonding, according to the present invention.

According to the invention, four variations of new approaches of soldering techniques are discribed in order to impart reliable bonding with universal solders. The types of universal solders that can be bonded well using the inventive techniques include Sn-Ag-RE, Au-Sn-RE, Sn-Sb-RE, Bi-Sn-RE, In-Sn-RE, In-Ag-RE, Sn-Ag-RE, and any other solder or braze alloys doped with 0.1 – 10% by weight, preferably 0.2 – 5 wt % of any one or more rare earth elements including mischmetal (a combination of La, Ce. Pr, etc.).

The inventive bonding techniques can be applicable to both the simple alloyed universal solders of various compositions described above, as well as the specially designed (rare earth buried) universal solders with buried rare earth structure. Various configuration of the universal solder that can be utilized are schematically illustrated in Fig. 1. The solder preform can be either a straight-forward alloy universal solder (Fig. 1(a)), a universal solder with a protective, oxidation-resistant novel metal film (Fig. 1(b)), a jacketed universal solder (Fig. 1(c)) or RE-buried solder (not shown),

or universal solder paste consisting of solder particles protected with novel metal coating (Fig. 1(d)).

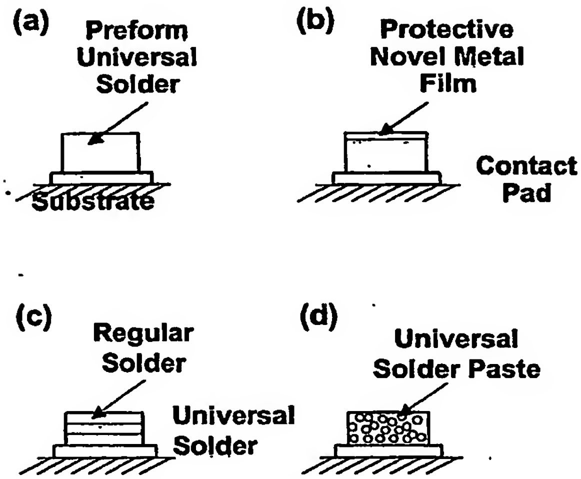

Fig. 1. Various univ. solder configurations.

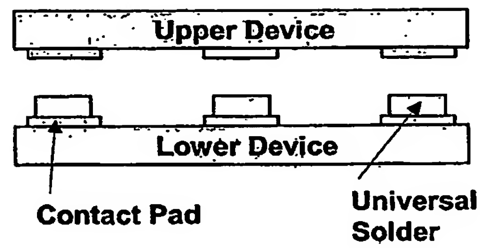

Fig. 2. Vertical interconnection using universal solder bonding.

The four inventive bonding processes using the universal solders, according to the invention, are as follows.

a). Vacuum bonding.
b). Rapid application of molten universal solder.
c). Controlled collapse joining with universal solder.
d). Rapid and localized heating by deposition of resistive heating element.

1. Vacuum Bonding

While solder bonding in vacuum is not a common practice, it can be a viable batch-type packaging process, e.g., for hermetic sealing of some MEMS, optical or electronic devices. The desired vacuum condition to enable the invention is a high vacuum of at least 10^{-6} torr, and preferably at least 10^{-7} torr, even more preferentially at least 5×10^{-8} torr. MEMS devices are micromachines by definition, and hence are relatively small in dimensions. For example, many MEMS devices to be bonded with a universal solder may be arranged, using automated assembly processing, on each of a multitude of shelves and placed in a vacuum chamber equipped with a capability to render either global or local heating. Each packaging assembly would have a lower device or substrate, preforms of a universal solder placed on contact pads or hermetic seal pads, and the upper device placed over the universal solder preforms with appropriate alignment and convenient fixturing array to maintain the alignment. The perform can be either bulk solder or thin film deposited solder. Such a process is illustrated in Fig. 2 for an exemplary vertical electrical interconnection.

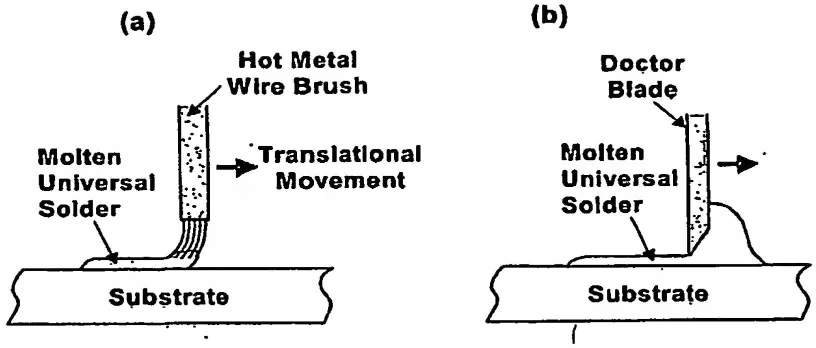

Fig. 3. Rapid application of universal solder by (a)hot wire brush, (b)doctor blade.

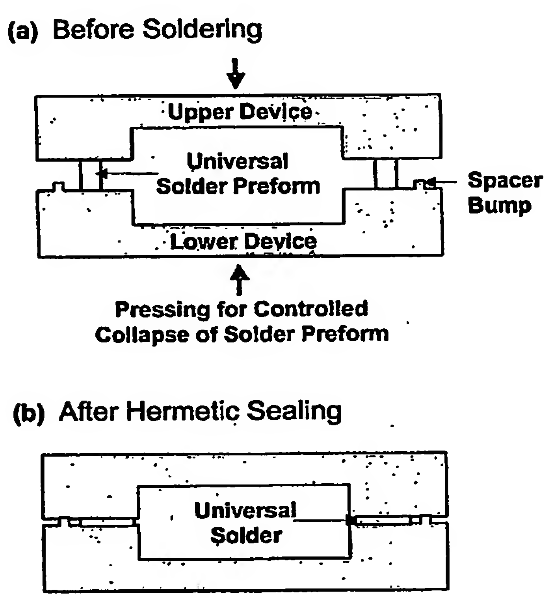

Fig. 4. Controlled collapse joining with universal solder.

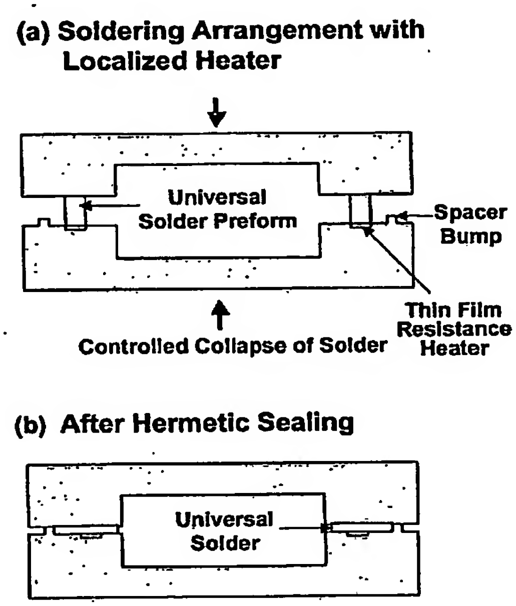

Fig. 5. Localized heater for controlled collapse joining with universal solder.

2. Rapid Application of Molten Universal Solder

For the inventive universal solder bonding process to produce successful solder bonding in oxygen-containing atmosphere such as the air, there is a time window of less than a few seconds to accomplish the wetting and joining before the oxidation of the universal solder takes place and an undesirable rare-earth-rich, gray colored oxide skin is formed to impede further wetting. One way of carrying out desirably rapid solder bonding is by introducing controlled and rapid application of molten solder, preferably by using automated processes. Carrying out such

an inventive process is preferably done in an inert gas atmosphere, although this is not an absolute requirment. As a demonstration of the principle (as illustrated in Fig. 3(a)), a hot metal brush can be utilized to pick up a volume of molten universal solder from a molten bath, quickly coat the substrate such as hermetic seal pads (pre-heated if necessary), and the upper device placed and pressed on top of the molten solder to form a joint. A natural air cooling or air blast may be used to initiate the solidification of the solder joint. An alternative scheme, Fig. 3(b), is to use a metallic doctor blade trailing a wire brush to produce a uniform solder layer thickness.

3. Controlled Collapse Joining with Universal Solder

If the undesirable oxide skin formed on the surface of molten universal solder can be broken off and fresh universal solder is released and immediately contacts the substrate surface, desired universal solder bonding can be achieved in air. This inventive process can be achieved by intentionally introducing mechanical disturbance as illustrated schematically in Fig. 4. Tall universal solder performs placed in the joint area are melted first, and then the upper device is pressed downward rapidly to collapse the molten universal solder so as to break the oxide skin and allow fresh solder to touch the device surface to be bonded. Small spacer bumps may be introduced if necessary to pre-set the solder joint thickness.

4. Rapid and Localized Heating by Deposition of Resistive Heating Element

It is always desirable to minimize the oxidation of molten solder surface. One way is to use vacuum or inert atmosphere as discussed earlier. Another way is to melt the solder rapidly and cut down the time of oxidation. Rapid heating can be obtained, for example, by incorporating resistive heating elements (e.g., thin film deposited Mo or W line on a portion of hermetic seal pad) and passing electrical current, as illustrated in Fig. 5. The heating element remains as a buried part of the solder joint material as the universal solder will also bond well to these elements.

The universal solder materials and bonding techniques described here can be useful for a variety of applications for various MEMS, optical and electronic devices packaging, especially for creating reliable hermetic sealing and flip-chip assembly without introducing complicated metallizations of various surfaces to be bonded. Examples of such devices assembled using the inventive universal solder materials and processes include bonding/assembly of bulk-fabricated MEMS multilayer structures such as an SOI(silicon-on-insulator)-fabricated, light-reflecting mirror layer, an electrode layer, and a spacer layer as illustrated in Fig. 6. See an article by R. Ryf, et al, "1296-Port MEMS Transparent Optical Crossconnect with 2.07 Petabits/s Switch Capacity", OFC'2001 (Optical Fiber Conference), Paper No. PD-28, March 17-22, 2001, Anaheim CA, USA.
Another example of the inventive assembled device, schematically illustrated in Fig. 7, is the hermetic sealing of optical MEMS assembly using universal solders. As the heat transfer in vacuum is known to be poor, the use of deposited thin film resistive heating element (as will be discussed below) can be combined with the vacuum bonding process to provide rapid heating of the universal solder. Yet another example is the bonding of optical fiber devices. The universal solders are directly solderable to optical fibers, and hence are technically useful for a variety of applications in optical communication devices such as illustrated in Fig. 8. Creep resistant solders, such as based on Sn-Ag-RE or Au-Sn-RE

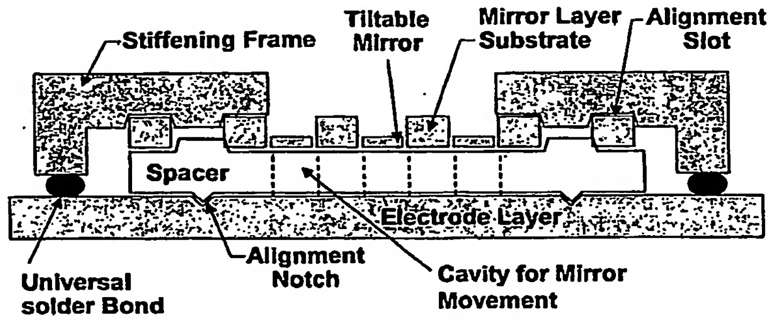

Fig. 6. Assembly of SOI layers with universal solder joints for optical MEMS.

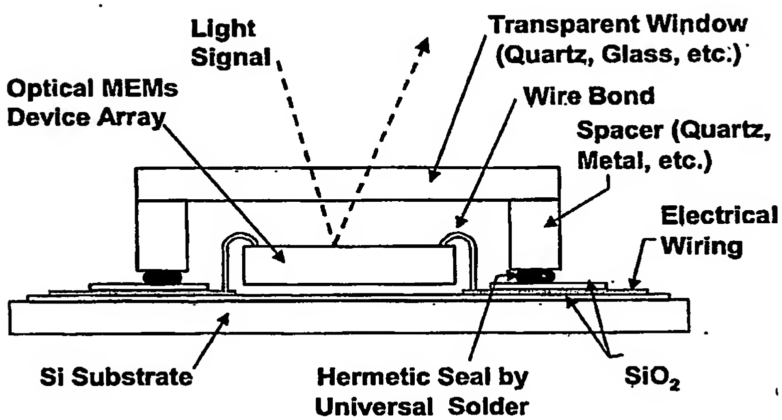

Fig. 7. Hermetic sealing for optical MEMS.

eutectic solders,are essential for securing and maintaining an optical alignment between the laser and the single mode optical fiber, where a tight, micrometer-level tolerance in dimensional stability is required. Fiber Bragg fiber gratings are SiO_2 based optical fiber devices with internal periodic refractive index purturbations along the fiber length corresponding to specific Bragg reflections for a certain wavelength of optical signals. They are frequently used for filtering specific, designated wavelength channels in wavelength-division-multiplexed optical communication systems. They need to be temperature-compensated to eliminate the fluctuation of refractive index of the grating with ambient temperature. One way of accomplishing this is to attach a negative CTE (coeffecient of thermal expansion) material. See articles by H. Mavoori and S. Jin, ""Low Thermal Expansion Copper Composites via Negative CTE Metallic Elements", JOM **50**(6), 70 (June, 1998) and by A. W. Sleight, A.W. *Nature* **389** (6654), 923 (1997). Figure 8(b) illustrates such an inventive device assembled by universal solder bonding of negative thermal expansion materials such as Ni-Ti or Zr-Tungstate on the elastically pre-strained fiber grating such that when the ambient temperature rises, the strain in the grating is reduced by the attached negative CTE material. The rare-earth containing solders can also be useful for convenient assembly of wavelength-tunable fiber gratings such as illustrated in Fig. 8(c). Such tunable optical fiber grating filter devices are described in an article by S. Jin, et al., "Broad-range, latchable reconfiguration of

Bragg wavelength in optical gratings", Appl. Phys. Lett. **74** (16), 2259 (1999). Other examples include hermetic sealing of RF relay MEMS switches [see an article by J. Kim, et al., "Integration and Packaging of MEMS Relays", SPIE Conf. Proc. on MEMS, May 2000, Paris, France] which can be useful for management of electronic data in automated test systems or control of communication information flow. The speed of movement of MEMS membranes, and hence the switching speed, is significantly reduced by air damping. For higher speed operations of such MEMS switches, hermetic sealing with vacuum environment is desirable. Hermetic sealing of such MEMS devices may involve simultaneous bonding to various surfaces such as Si, insulators like SiO_2, SiN_x, and electrical wiring made of poly Si or Al lines. Universal solders have desirable characteristics of being able to bond to all these different surfaces simultaneously during hermetic sealing.

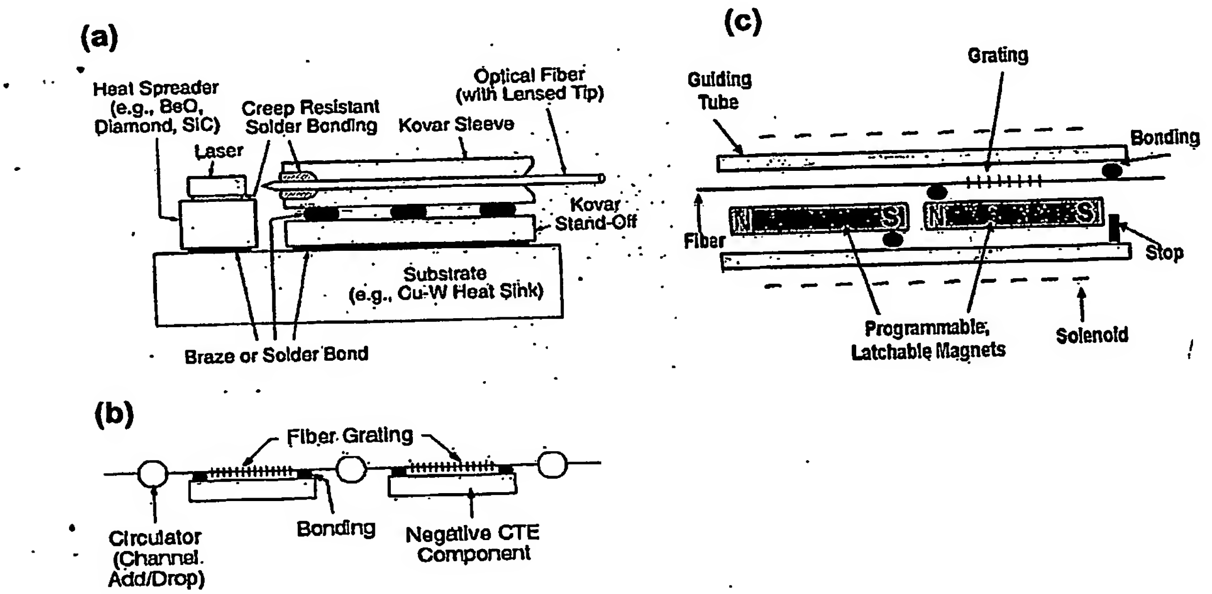

Fig. 8. Optical fiber bonding for (a) fiber positioning in alignment with laser beam, (b) temperature-compensators, (c) wavelength-tunable fiber grating filter device.